PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference IR-3224C-PCT	**FOR FURTHER ACTION** see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/US92/10873	International filing date *(day/month/year)* 21 DECEMBER 1992	(Earliest) Priority Date *(day/month/year)* 26 DECEMBER 1991
Applicant ELF ATOCHEM NORTH AMERICA, INC.		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 2 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. [ ] **Certain claims were found unsearchable** (See Box I).

2. [ ] **Unity of invention is lacking** (See Box II).

3. [ ] The international application contains disclosure of a **nucleotide and/or amino acid sequence listing** and the international search was carried out on the basis of the sequence listing
   - [ ] filed with the international application.
   - [ ] furnished by the applicant separately from the international application,
     - [ ] but not accompanied by a statement to the effect that it did not include matter going beyond the disclosure in the international application as filed.
   - [ ] transcribed by this Authority.

4. With regard to the **title**,
   - [X] the text is approved as submitted by the applicant.
   - [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,
   - [X] the text is approved as submitted by the applicant.
   - [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is:

   Figure No. ______
   - [ ] as suggested by the applicant.
   - [ ] because the applicant failed to suggest a figure.
   - [ ] because this figure better characterizes the invention.
   - [ ] None of the figures.

INTERNATIONAL SEARCH REPORT

PCT/US92/10873

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :G01G 19/02; C07F 7/22
US CL :106/287.16; 252/305; 106/287.24
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 106/287.16;252/305;106/287.24

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	SU, A, 0833649 05 June 1981, See abstract.	1-5,11-13, 16-26
Y	JA, A, 58-189263 (HITACHI CHEMICAL) 04 November 1983, See abstract.	6,14,15
Y	JA, A, 57-34164 (KANSAI PAINT) 24 February 1982, See abstract.	1-5,7,11-13, 15-26
Y	US, A, 4,227,929 (LAW ET AL) 14 October 1980 See abstract, column 4, line 15 through column 8, line 15.	1-5,7-13, 16-26

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be part of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 FEBRUARY 1993	05 MAR 1993

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	DAVID M. BRUNSMAN
Facsimile No. NOT APPLICABLE	Telephone No. (703) 308-0662

Copy for the designated Office (D US)

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92*bis*.1 and Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

HENN, Robert, B.
Elf Atochem North America, Inc.
Patent Department, 26th Floor
2000 Market Street
Philadelphia, PA 19103-3222
ETATS-UNIS D'AMERIQUE

Date of mailing (*day/month/year*) 23 August 1993 (23.08.93)	
Applicant's or agent's file reference IR-3224C-PCT	**IMPORTANT NOTIFICATION**
International application No. PCT/US92/10873	International filing date (*day/month/year*) 21 December 1992 (21.12.92)

1. The following indications appeared on record concerning:

☐ the applicant ☐ the inventor ☒ the agent ☐ the common representative

Name and Address	State of Nationality	State of Residence
HENN, Robert, B. Elf Atochem North America, Inc. Three Parkway Philadelphia, PA 19102-1303 United States of America	Telephone No. Facsimile No. Teleprinter No.	

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person ☐ the name ☒ the address ☐ the nationality ☐ the residence

Name and Address	State of Nationality	State of Residence
HENN, Robert, B. Elf Atochem North America, Inc. Patent Department, 26th Floor 2000 Market Street Philadelphia, PA 19103-3222 United States of America	Telephone No. 215/419-7792 Facsimile No. Teleprinter No.	

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

☒ the receiving Office
☐ the International Searching Authority
☐ the International Preliminary Examining Authority
☒ the designated Offices concerned
☐ the elected Offices concerned
☐ other:

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. (41-22) 740.14.35	Authorized officer L. Schwarz Telephone No. (41-22) 730.91.11

Form PCT/IB/306 (July 1992)

HOME COPY

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only	
International Application No.	PCT/US 92/10873
International Filing Date	21 DEC 1992
Name of receiving Office and "PCT International Application"	PCT INTERNATIONAL APPLICATION RO/US

Applicant's or agent's file reference *(if desired) (12 characters maximum)* IR-3224C-PCT

Box No. I TITLE OF INVENTION

COATING COMPOSITION FOR GLASS

Box No. II APPLICANT

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

ELF ATOCHEM NORTH AMERICA, INC.
Three Parkway
Philadelphia, Pennsylvania 19102-1303
United States of America

☐ This person is also inventor.

Telephone No. (215) 587-7000

Facsimile No. (215) 587-7075

Teleprinter No.

State (*i.e. country*) of nationality: US

State (*i.e. country*) of residence: US

This person is applicant for the purposes of: [X] all designated States [X] all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Box No. III FURTHER APPLICANTS AND/OR (FURTHER) INVENTORS

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

RUSSO, David A.
22 Brenda Lane
Norristown, Pennsylvania 19403-2002
United States of America

This person is:
☐ applicant only
[X] applicant and inventor
[X] inventor only *(If this check-box is marked, do not fill in below.)*

State (*i.e. country*) of nationality:

State (*i.e. country*) of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America [X] the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

DIRKX, Ryan R.
2006 Turnberry Circle
Glenmoore, Pennsylvania 19343
United States of America

This person is:
☐ applicant only
[X] applicant and inventor
[X] inventor only *(If this check-box is marked, do not fill in below.)*

State (*i.e. country*) of nationality:

State (*i.e. country*) of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America [X] the United States of America only ☐ the States indicated in the Supplemental Box

[X] Further applicants and/or (further) inventors are indicated on a continuation sheet.

See Notes to the request form

Continuation of Box No. III FURTHER APPLICANTS AND/OR (FURTHER) INVENTORS

If none of the following sub-boxes is used, this sheet is not to be included in the request.

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

FLORCZAK, Glenn P.
2 Hilltop Boulevard
East Brunswick, New Jersey 08816-2831
United States of America

This person is:
- [ ] applicant only
- [X] applicant and inventor
- [X] inventor only *(If this check-box is marked, do not fill in below.)*

State *(i.e. country)* of nationality:

State *(i.e. country)* of residence:

This person is applicant for the purposes of: [ ] all designated States [ ] all designated States except the United States of America [X] the United States of America only [ ] the States indicated in the Supplemental Box

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

This person is:
- [ ] applicant only
- [ ] applicant and inventor
- [ ] inventor only *(If this check-box is marked, do not fill in below.)*

State *(i.e. country)* of nationality:

State *(i.e. country)* of residence:

This person is applicant for the purposes of: [ ] all designated States [ ] all designated States except the United States of America [ ] the United States of America only [ ] the States indicated in the Supplemental Box

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

This person is:
- [ ] applicant only
- [ ] applicant and inventor
- [ ] inventor only *(If this check-box is marked, do not fill in below.)*

State *(i.e. country)* of nationality:

State *(i.e. country)* of residence:

This person is applicant for the purposes of: [ ] all designated States [ ] all designated States except the United States of America [ ] the United States of America only [ ] the States indicated in the Supplemental Box

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

This person is:
- [ ] applicant only
- [ ] applicant and inventor
- [ ] inventor only *(If this check-box is marked, do not fill in below.)*

State *(i.e. country)* of nationality:

State *(i.e. country)* of residence:

This person is applicant for the purposes of: [ ] all designated States [ ] all designated States except the United States of America [ ] the United States of America only [ ] the States indicated in the Supplemental Box

[ ] Further applicants and/or (further) inventors are indicated on another continuation sheet.

DELETED BY RO/US

92/10273

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: [X] agent [ ] common representative

Name and address: *(Family name followed by given name: for a legal entity, full official designation. The address must include postal code and name of country.)*

HENN, Robert B.; MARCUS, Stanley A.; of
ELF ATOCHEM NORTH AMERICA, INC.
Three Parkway
Philadelphia, Pennsylvania 19102-1303
United States of America

Telephone No. (215) 587-7000

Fascimile No. (215) 587-7075

Teleprinter No.

[ ] Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Box No. V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) *(mark the applicable check-boxes; at least one must be marked)*:

Regional Patent

[X] **EP** **European Patent:** **AT** Austria, **BE** Belgium, **CH** and **LI** Switzerland and Liechtenstein, **DE** Germany, **DK** Denmark, **ES** Spain, **FR** France, **GB** United Kingdom, **GR** Greece, **IT** Italy, **LU** Luxembourg, **MC** Monaco, **NL** Netherlands, **SE** Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT

[ ] **OA** **OAPI Patent:** Benin, Burkina Faso, Cameroon, Central African Republic, Chad, Congo, Côte d'Ivoire, Gabon, Guinea, Mali, Mauritania, Senegal, Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT *(if other kind of protection or treatment desired, specify on dotted line)* ....

National Patent *(if other kind of protection or treatment desired, specify on dotted line)*:

[ ] **AT** Austria
[X] **AU** Australia
[ ] **BB** Barbados
[ ] **BG** Bulgaria
[X] **BR** Brazil
[X] **CA** Canada
[ ] **CH and LI** Switzerland and Liechtenstein
[X] **CS** Czechoslovakia
[ ] **DE** Germany
[ ] **DK** Denmark
[ ] **ES** Spain
[ ] **FI** Finland
[ ] **GB** United Kingdom
[X] **HU** Hungary
[X] **JP** Japan
[ ] **KP** Democratic People's Republic of Korea
[X] **KR** Republic of Korea
[ ] **LK** Sri Lanka
[ ] **LU** Luxembourg
[ ] **MG** Madagascar
[ ] **MN** Mongolia
[ ] **MW** Malawi
[ ] **NL** Netherlands
[X] **NO** Norway
[X] **PL** Poland
[ ] **RO** Romania
[X] **RU** Russian Federation
[ ] **SD** Sudan
[ ] **SE** Sweden
[X] **US** United States of America
continuation-in-part

Check-boxes reserved for designating States (for the purposes of a national patent) which have become party to the PCT after issuance of this sheet:

[X] New Zealand
[ ] ....
[ ] ....
[ ] ....

In addition to the designations made above, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except the designation(s) of ________.
The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. *(Confirmation of a designation consists of the filing of a notice specifying that designation and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.)*

Supplemental Box *If the Supplemental Box is not used, this sheet need not be included in the request.*

Use this box in the following cases:

1. If, in any of the Boxes, the space is insufficient to furnish all the information: *in such case, write "Continuation of Box No. ..." [indicate the number of the Box] and furnish the information in the same manner as required according to the captions of the Box in which the space was insufficient;*

in particular:

(i) *if more than three persons are involved as applicants and/or inventors and no "continuation sheet" is available:* *in such case, write "Continuation of Box No. III" and indicate for each additional person the same type of information as required in Box No. III;*

(ii) *if, in Box No. II or in any of the sub-boxes of Box No. III, the indication "the States indicated in the Supplemental Box" is checked:* *in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the applicant(s) involved and, next to (each) such name, the State or States (and/or, where applicable, European or OAPI patent) for the purposes of which the named person is applicant;*

(iii) *if, in Box No. II or in any of the sub-boxes of Box No. III, the inventor or the inventor/applicant is not inventor for the purposes of all designated States or for the purposes of the United States of America:* *in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the inventor(s) and, next to (each) such name, the State or States (and/or, where applicable, European or OAPI patent) for the purposes of which the named person is inventor;*

(iv) *if, in addition to the agent(s) indicated in Box No. IV, there are further agents:* *in such case, write "Continuation of Box No. IV" and indicate for each further agent the same type of information as required in Box No. IV;*

(v) *if, in Box No. V, the name of any State (or OAPI) is accompanied by the indication "patent of addition," "certificate of addition," or "inventor's certificate of addition," or if, in Box No. V, the name of the United States of America is accompanied by an indication "Continuation" or "Continuation-in-part":* *in such case, write "Continuation of Box No. V" and the name of each State involved (or OAPI), and after the name of each such State (or OAPI), the number of the parent title or parent application and the date of grant of the parent title or filing of the parent application;*

(vi) *if there are more than three earlier applications whose priority is claimed:* *in such case, write "Continuation of Box No. VI" and indicate for each additional earlier application the same type of information as required in Box No. VI.*

2. If the applicant claims, in respect of any designated Office, the benefits of provisions of the national law concerning non-prejudicial disclosures or exceptions to lack of novelty: *in such case, write "Statement Concerning Non-Prejudicial Disclosures or Exceptions to Lack of Novelty" and furnish that statement below.*

United States of America [Application No] 07/814,366
[filed] 26 December 1991 (26.12.91)

United States of America [Application No] 07/814,352
[filed] 27 December 1991 (27.12.91)

DELETED BY RO/US

Box No. VI PRIORITY CLAIM — Further priority claims are indicated in the Supplemental Box ☐

The priority of the following earlier application(s) is hereby claimed:

	Country (in which, or for which, the application was filed)	Filing Date (day/month/year)	Application No.	Office of filing (only for regional or international application)
(1)	US	26 December 1991 (26.12.91)	07/814,366	
(2)	US	27 December 1991 (27.12.91)	07/814,352	
(3)				

Mark the following check-box if the certified copy of the earlier application is to be issued by the Office which for the purposes of the present international application is the receiving Office (a fee may be required):

[X] The receiving Office is hereby requested to transmit to the International Bureau a certified copy of the earlier application(s) identified above at item(s) : (1), (2)

Box No. VII EARLIER SEARCH

Fill in where a search (international, international-type or other) by the International Searching Authority has already been carried out or requested and the Authority is now requested to base the international search, to the extent possible, on the results of that earlier search. Identify such search or request either by reference to the relevant application (or the translation thereof) or by reference to the search request:

Country (or regional Office):	Date (day/month/year):	Number:
US	26 December 1991 (26.12.91)	07/814,366
US	27 December 1991 (27.12.91)	07/814,352

Box No. VIII CHECK LIST

This international application contains the following number of sheets:

1. request	:	5 sheets
2. description	:	15 sheets
3. claims	:	3 sheets
4. abstract	:	1 sheets
5. drawings	:	0 sheets
Total	:	24 sheets

This international application is accompanied by the item(s) marked below:

1. [ ] separate signed power of attorney
2. [ ] copy of general power of attorney
3. [ ] statement explaining lack of signature
4. [ ] priority document(s) *(specify)*:
5. [X] fee calculation sheet
6. [ ] separate indications concerning deposited microorganisms
7. [ ] nucleotide and/or amino acid sequence listing
8. [ ] other *(specify)*:

Figure No. ________ of the drawings (if any) should accompany the abstract when it is published.

Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

Robert B. Henn

(Robert B. HENN)

Stanley A. Marcus

[(Stanley A. MARCUS, Deputy General Counsel - Patents)]

For receiving Office use only

1. Date of actual receipt of the purported international application:	11 Rec'd PCT/PTO 21 DEC 1992
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:	
4. Date of timely receipt of the required corrections under PCT Article 11(2):	
5. International Searching Authority specified by the applicant: ISA /	6. [ ] Transmittal of search copy delayed until search fee is paid

2. Drawings:
[ ] received :
[ ] not received:

For International Bureau use only

Date of receipt of the record copy by the International Bureau:

DELETED BY RO/US

This sheet is not part of and does not count as a sheet of the international application.

PCT

FEE CALCULATION SHEET
Annex to the Request

For receiving Office use only

International application No. PCT/US 92/10873

Date stamp of the receiving Office

Applicant's or agent's file reference: IR-3224C-PCT

Applicant

ELF ATOCHEM NORTH AMERICA, INC.

CALCULATION OF PRESCRIBED FEES

1. TRANSMITTAL FEE . . . . 200 [T] 200
2. SEARCH FEE . . . . 410 [S] 410

International search to be carried out by USPTO

(If two or more International Searching Authorities are competent in relation to the international application, indicate the name of the Authority which is chosen to carry out the international search.)

3. INTERNATIONAL FEE

Basic Fee

The international application contains 19 sheets.

first 30 sheets . . . . 593 [b_1] 593

____ x 12 = ____ [b_2]
remaining sheets x additional amount

Add amounts entered at b_1 and b_2 and enter total at B . . . . 593 [B] 593

Designation Fee

13 x 144 = 1440 [D] 1440
number of designations x amount of designation fee

(If that total exceeds the figure which corresponds to the amount of the designation fee multiplied by ten, enter the latter figure in box D.)

Add amounts entered at B and D and enter total at I . . . . 2033 [I] 2033

4. FEE FOR PRIORITY DOCUMENT . . . . 24 [P] 24
5. TOTAL FEES PAYABLE

Add amounts entered at T, S, I and P, and enter total in the TOTAL box . . . . 2667 TOTAL 2667

☐ The designation fee is not paid at this time.

MODE OF PAYMENT

☒ authorization to charge deposit account (see below)	☐ bank draft	☐ coupons
☐ cheque	☐ cash	☐ other *(specify)*:
☐ postal money order	☐ revenue stamps	

DEPOSIT ACCOUNT AUTHORIZATION

The RO/ US

☒ is hereby authorized to charge the total fees indicated above to my deposit account.

☒ is hereby authorized to charge any deficiency or credit any overpayment in the total fees indicated above to my deposit account.

☒ is hereby authorized to charge the fee for preparation and transmittal of the priority document to the International Bureau of WIPO to my deposit account.

01-2717
Deposit Account Number

December 18, 1992
Date *(day/month/year)*

Robert B. Henn
Signature Robert B. Henn

Form PCT/RO/101 (Annex) (July 1992)

See Notes to the fee calculation sheet

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification [5] :
G01G 19/02, C07F 7/22

A1

(11) International Publication Number: WO 93/13393

(43) International Publication Date: 8 July 1993 (08.07.93)

(21) International Application Number: PCT/US92/10873

(22) International Filing Date: 21 December 1992 (21.12.92)

(30) Priority data:
07/814,366 26 December 1991 (26.12.91) US
07/814,352 27 December 1991 (27.12.91) US

(60) Parent Applications or Grants
(63) Related by Continuation
US 07/814,366 (CIP)
Filed on 26 December 1991 (26.12.91)
US 07/814,352 (CIP)
Filed on 27 December 1991 (27.12.91)

(71) Applicant *(for all designated States except US)*: ELF ATOCHEM NORTH AMERICA, INC. [US/US]; Three Parkway, Philadelphia, PA 19102-1303 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : RUSSO, David, A. [US/US]; 22 Brenda Lane, Norristown, PA 19403-2002 (US). DIRKX, Ryan, R. [US/US]; 2006 Turnberry Circle, Glenmoore, PA 19343 (US). FLORCZAK, Glenn, P. [US/US]; 2 Hilltop Boulevard, East Brunswick, NJ 08816-2831 (US).

(74) Agents: HENN, Robert, B. et al.; Elf Atochem North America, Inc., Three Parkway, Philadelphia, PA 19102-1303 (US).

(81) Designated States: AU, BR, CA, CS, HU, JP, KR, NO, NZ, PL, RU, US , European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: COATING COMPOSITION FOR GLASS

(57) Abstract

A composition for coating glass by chemical-vapor deposition comprises a mixture of a tin oxide precursor monobutyltin trichloride, a silicon dioxide precursor tetraethylorthosilicate, and an accelerant such as triethyl phosphite; the composition is gaseous below 200 °C, and permits coating glass having a temperature from 450 to 650 °C at deposition rates higher than 350 Å/sec. The layer of material deposited can be combined with other layers to produce an article with specific properties such as controlled emissivity, refractive index, abrasion resistance, or appearance.

PCT/US 92/10873
RO/US 12 FEB 1993
08/104125
17 Rec'd PCT/PTO 21 DEC 1992

COATING COMPOSITION FOR GLASS

BACKGROUND OF THE INVENTION

Cross-Reference to Related Application. This application is a continuation-in-part of our copending United States Patent Applications, Serial Numbers 07/814,366, filed 12/26/91 and 07/814,352, filed 12/27/91.

Field of the Invention. The present invention is in the field of coatings on substrates. More particularly, this invention is in the field of compositions for the deposition of coatings at high rates on glass or glass articles to provide controlled refractive index, improved emissivity characteristics, and/or appearance and abrasion resistance, and to complement or enhance other properties.

Description of the Prior Art. Transparent semi-conductor films such as indium oxide, cadmium stannate, or doped tin oxide, can be applied to various transparent substrates such as, e.g., soda-lime glasses, in order to reflect long-wavelength infrared radiation. Transparent dielectric films such as titanium dioxide or undoped tin oxide can be applied to transparent articles such as glass bottles to form a base coat for a second coating with a specific function. Depending on the thickness of the semiconductor or dielectric film, various reflected iridescent colors may be observed. This iridescent effect is considered to be detrimental to the appearence of the glass in applications such as windows with low emissivity, or bottles for food or beverages.

Methods and apparatus for coating glass, and especially continuous coating on moving glass, are known in the art. A description of apparatus useful in preparing a coated-glass article is found in Lindner, U.S. 4,928,627, made a part of this disclosure by reference herein.

Various procedures have been devised for reducing or eliminating iridescence. For the low-emissivity application, Zaromb, in US 3,378,396, describes an article comprising a transparent glass substrate coated with tin and silicon oxides; the coating varies gradually in composition from a high ratio of silicon oxide to tin oxide at the substrate surface, gradually changing to almost pure tin oxide, and changing further to a ratio of not more than

60% silicon oxide to not less than 40% tin oxide at the interface of that coating with the atmosphere. The refractive index of the coating nearest to the substrate is about 1.5, substantially the refractive index of silica glass, and changes to about 2.0, the refractive index of tin oxide, at the air interface, providing an intermediate coating layer without an optical interface. The article so coated has little to no iridescence in reflected light. Zaromb teaches that aqueous solutions of tin and silicon chlorides can be spray-applied to achieve his coatings. Spray applications are usually batch operations which do not yield high-quality, uniform films; there is no mention of other means of application such as chemical-vapor deposition (CVD). He also fails to give any indication of the deposition rate, a key parameter for a commercial industrial application.

Another approach is described by Gordon in US 4,187,336. One or more layers of a transparent material with a refractive index intermediate between that of a glass substrate and a conductive tin oxide film are deposited by atmospheric-pressure CVD between the glass and the tin oxide film. It is necessary for the intermediate layers to have specific refractive indices and thicknesses in order to be effective. It is noted that when the intermediate films contained silicon dioxide, suitable volatile compounds were found to be silane, dimethysilane, diethylsilane, tetramethyl silane, and the silicon halides. No other precursors are mentioned. The deposition rates obtained for the processes described were on the order of from 10 to 20 Ångstroms per second (Å/sec.). Such rates are an order of magnitude below those necessary for a commercial industrial process.

In United States Patent 4,206,252, Gordon describes a process for depositing mixed oxide and nitride coating layers of continuously varying refractive index between a glass substrate and an infra-red-reflecting coating, whereby the film iridesence is eliminated. When silicon dioxide is part of the mixed oxide film, the patent teaches that volatile silicon compounds with Si-Si and Si-H bonds are suitable precursors. Compounds such as 1,1,2,2-tetramethyldisilane, 1,1,2-trimethyldisilane, and 1,2-dimethyldisilane are

disclosed. All of the compounds containing Si-Si and Si-H bonds to which reference is made are expensive, and none are comercially available.

In U.S. 4,386,117, Gordon describes a process for preparing mixed silicon oxide/tin oxide coatings at specific refractive indices or a continuous gradient as taught by Zaromb in US 3,378,396, at optimum deposition rates of 80 to 125 Å/sec, using alkoxy-peralkylpolysilane precursors such as methoxypentamethyldisilane or dimethoxytetramethyldisilane. Again, the silica precursors cited and inferred are impractical for industrial use, because none of them is commercially available on a large scale.

Lagendijk, in United States Patent 5,028,566, notes in column 4 that tetraethyl orthosilicate (TEOS) suffers from a number of disadvantages in its application to a substrate by low-pressure CVD; that is, a pressure of about 500 milliTorr. These disadvantages include difficulty of doping the resultant film with phosphorus, and controlled-source delivery due to the low vapor pressure of TEOS. Lagendijk also points out that attempts at an all-liquid process to produce borophosphosilicate glass have met with limited success. He further equates the dopant effect within a broad range of phosphorus, boron, antimony, arsenic and chromium compounds, but only when used with silicon compounds having no carbon-oxygen-silicon bonds, and two or more silicon atoms.

In bottle applications, the coatings are applied at such low thicknesses, i.e., about 100 Å, that no iridescence is possible. However, the films are not continuous, and this discontinuity makes them unsuitable for other applications. One solution to the discontinuity is to deposit thicker films of a material with a refractive index closer to that of the article. A mixed metal oxide/silicon oxide material deposited at a significantly more rapid rate than has heretofore been achieved would be desirable, as discussed further hereinbelow.

All the silanes disclosed in the prior art for making mixed metal oxide/silicon dioxide coatings have certain features which make them unsatisfactory for commercial development. Some are very corrosive, flammable, or oxygen-sensitive, and require special handling. Others are not readily available, or

are too expensive for commercial use. Of the materials which can be used, the biggest problem which limits their commercial development in mixed metal oxide/silicon oxide and/or oxynitride intermediate layers has been that of inadequate deposition rates. When the substrate is flat glass and the deposition process is CVD at ambient pressure, the deposition rate of the intermediate layers must be high enough to coat a production-line glass ribbon traveling at line speeds as high as about 15 meters per minute (m/min). Rates for deposition of the desired layers of about 350Å are desirable, and rates on the order of 400 to 600 Å/sec are preferable. Such rates have not heretofore been achieved under conditions which permit continuous, mass production of glass with properties.

To overcome the problems as discussed hereinabove, silica precursors are needed which are inexpensive, readily available, easy to handle, and have adequate deposition rates when vaporized with metal oxide precursors. Alkoxysilanes such as TEOS, a commodity chemical, would be desirable. However, prior to the present invention, it has not been possible to deposit silicon oxide films from TEOS by atmospheric-pressure CVD at commercially acceptable deposition rates, except at temperatures at or above 700 degrees Celsius (°C). Some success has been achieved at temperatures of from about 450 to about 680°C, but only by modifying the atmospheric-pressure CVD process through plasma enhancement or reduced pressure, neither of which is generally acceptable for commerical use on a continuous glass ribbon. Additives such as oxygen, ozone, or trimethyl phosphite have also been used in these modified processes, but the rates achieved are still lower than those needed for an effective commercial system.

D. S. Williams and E. A. Dein, in *J. Electrochem. Soc. 134(3) 657-64 (1987)*, showed that phosphosilicate and borophosphosilicate glass films with controllable refractive index can be deposited at rates of about 200 Å/sec between 515 and 680°C by the low-pressure CVD of TEOS with phosphorous or boron oxides in concentrations which varied as a function of the additive used. The low-pressure process described here is not amenable to a continuous on-line application of oxides.

In *Proceedings, 2nd International ULSI Science and Technical Symposium, ECS Proceedings Vol. 98(9), 571-78 (1989)*, D. A. Webb et al. reported that silicon oxide films could be deposited from TEOS at rates of about 125 Å/sec in a plasma-enhanced CVD process using oxygen. However, plasma-enhanced CVD is not a viable option for the continuous commmercial application of oxide films to glass, being a batch process requiring complex and costly low-pressure apparatus.

A. K. Hochberg and D. L. O'Meara in *J. Electrochem. Soc. 136(6) 1843 (1989)* reported enhanced deposition of silicon oxide films at 570°C by CVD at low pressure when trimethylphosphite was added to TEOS. As with plasma-enhanced CVD, however, low-pressure CVD is not readily utilized for the continuous commercial application of silicon-oxide films on a moving glass sheet to produce a coated-glass article, due at least in part to the cost and complexity of the device used for deposition at low pressure.

From a review of the prior art, it cannot be determined what precursor combinations, if any, can be used for continuous deposition, under conditions and at a rate suitable for mass production, of mixed metal oxide/silicon oxide films at adequate rates from readily available and relatively inexpensive reagents.

Primary or secondary coatings on glass substrates are further useful to enhance or complement properties of either the substrate or one or more of the coatings thereon, improvement of iridesence being only one application. Other uses of coatings include, e.g., protection of the substrate surface from abrasion, addition of color to clear glass, and screening of particular wavelengths of incident radiation.

DISCUSSION OF THE INVENTION

This invention is a gaseous composition for producing an improved coating on glass, wherein the coated glass exhibits specific properties such as, e.g., controlled refractive index, abrasion resistance, color enhancement, low emissivity, selective light filtration, and anti-iridescence on flat-glass substrates. The invention is made by CVD at rates greater than about 350Å/sec. at atmospheric pressure and at temperatures lower than 700°C, by using a

mixture which includes at least one precursor for a metal oxide, selected from the group consisting of volatile compounds of tin, germanium, titanium, aluminum, zirconium, zinc, indium, cadmium, hafnium, tungsten, vanadium, chromium, molybdenum, iridium, nickel and tantalum. The gaseous composition further includes a precursor for silicon dioxide, and one or more additives selected from the group consisting of phosphites, borates, water, alkyl phosphine, arsine and borane derivatives; PH_3, AsH_3 and B_2H_6; and O_2, N_2O, NF_3, NO_2 and CO_2. The additives are termed "accelerants" herein; the accelerants serve to increase the rate of deposition of the film onto the glass from the mixture. The mixture of precursors and additives is gaseous under the conditions of application required to produce the coated-glass article; the reaction of the materials in the gaseous mixture with atmospheric or added oxygen provides the corresponding oxides which are deposited on the glass substrate.

Those skilled in the art will understand that precursors and materials discussed in this specification must be sufficiently volatile, alone or with other materials, and sufficiently stable under the conditions of deposition, to be a part of the composition from which the desired films are deposited.

Precursors for deposition of metal oxides include, e.g., aluminum alkyls and alkoxides, cadmium alkyls, germanium halides and alkoxides, indium alkyls, titanium halides, zinc alkyls, and zirconium alkoxides. Specific examples of such compounds include, e.g., $Al(C_2H_5)_3$, CrO_2Cl_2, $GeBr_4$, $Ti(OC_3H_7)_4$, $TiCl_4$, $TiBr_4$, $Ti(C_5H_7O_2)_4$, $Zr(OC_5H_9)_4$, $Ni(CO)_4$, VCl_4, $Zn(CH_3)_2$, $Zr(C_5H_9O)_4$, and the like.

Tin precursors include those described by the general formula R_nSnX_{4-n}, where R is independently chosen from straight, cyclic, or branched-chain alkyl or alkenyl of from one to about six carbons; phenyl, substituted phenyl, or $R'CH_2CH_2$-, where R' is MeO_2C-, EtO_2C-, CH_3CO-, or HO_2C-; X is selected from the group consisting of halogen, acetate, perfluoroacetate, and their mixtures; and where n is 0, 1, or 2. Preferred precursors for tin oxide in the article of this invention are the organotin halides.

Precursors for silicon oxide include those described by the general formula $R_mO_nSi_p$, where *m* is from 3 to 8, *n* is from 1 to 4, *p* is from 1 to 4, and *R* is independently chosen from hydrogen and acyl, straight, cyclic, or branched-chain alkyl and substituted alkyl or alkenyl of from one to about six carbons, and phenyl or substituted phenyl. Preferred precursors for silicon oxide include tetraethylorthosilicate, diacetoxydi-t-butoxysilane, ethyltriacetoxysilane, methyltriacetoxysilane, methyldiacetoxylsilane, tetramethyldisiloxane, tetramethylcyclotetrasiloxane, dipinacoloxysilane, 1,1-dimethylsila-2-oxacyclohexane, tetrakis (1-methoxy-2-propoxy) silane, and triethoxysilane.

Suitable accelerants include phosphite and borate derivatives of the general formula $(R''O)_3P$ and $(R''O)_3B$, where R" is independently chosen from straight, cyclic, or branched-chain alkyl or alkenyl of from one to about six carbons; phenyl, substituted phenyl, or $R'''CH_2CH_2$-, where R"' is MeO_2C-, EtO_2C-, CH_3CO-, or HO_2C-; R" is preferably alkyl or alkenyl of from 1 to 4 carbons in length. Particularly preferred accelerants are those selected from the group consisting of boron and phosphorus esters; most preferred are TEB and TEP.

The precursors to the overcoated layer comprise MBTC or any of the organotins described by the general formula R_nSnX_{4-n} above, and a material chosen to impart a semi-conductive property to the tin oxide; such materials include, e.g., antimony compounds such as trimethylantimony, phosphorous compounds such as triethylphosphine, and fluorine-containing compounds such as trifluoroacetic acid, trifluoroacetic anhydride, ethyl trifluoroacetate, 2,2,2-trifluoroethanol, ethyl 4,4,4-trifluoroacetoacetone, heptafluorobutyryl chloride, and hydrogen fluoride. The tin oxide layer can also be made conductive by depositing sub-stoichiometric films having the composition SnO_{2-x}, wherein x is a non-integer having a value between zero and 1, and wherein the value of x can vary within a given film. The materials for imparting semi-conductive properties to the tin oxide can also be added to the precursors for the first layer, to enhance the emissivity of the entire coating system , i.e., the emissivity of the combined first and second layers.

Those skilled in the art will realize that the tin oxide can be replaced in these films entirely or in part by the oxides of other metals such as, e.g., germanium, titanium, aluminum, zirconium, zinc, indium, cadmium, hafnium, tungsten, vanadium, chromium, molybdenum, iridium, nickel and tantalum.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The preferred embodiment of the present invention is a gaseous composition at a temperature below about 200°C at atmospheric pressure, adapted to deposit a film of tin oxide and silicon oxide at a rate greater than about 350Å/sec. which comprises a precursor of tin oxide, a precursor of silicon oxide, an accelerant selected from the group consisting of organic phosphites, organic borates and water, and mixtures thereof, and a source of oxygen.

In another embodiment of this invention, the composition results in a film deposited at atmospheric pressure wherein the film comprises one or more mixed metal oxide/silicon dioxide films on a glass substrate, the deposition being made from a mixture comprising a metal oxide precursor, a silicon dioxide precursor, and at least one additive which improves or accelerates the deposition rate significantly when compared to the deposition rate without the additive. The deposited films can contain additional oxides related to the additives used. Further, the deposited mixed oxide films can have specific properties in their own right such as, e.g., designed refractive index, or can be combined with other films, under- or overcoated, or both, to have a combined property such as, e.g., color neutrality or lubricity.

In a more-preferred embodiment, the composition provides a mixed metal oxide/silicon dioxide film comprising multiple tin oxide/silicon dioxide layers of, e.g., increasing refractive index; further, a chosen property of a given layer, such as, e.g., the refractive index, can vary continuously such that an overcoated layer of tin oxide will have minimal reflected color. A given layer may thus have a concentration of silicon oxide and tin oxide different from the concentrations of silicon oxide and tin oxide in an adjacent layer. The films can also contain oxides of the accelerants, particularly when the additives contain phosphorus or boron.

In a most-preferred embodiment of the composition of this invention, the precursors to the mixed oxide layer comprise organotin halides generally and monobutyltin trichloride (MBTC) in particular, TEOS, and the accelerant triethyl phosphite (TEP).

The compositions of the films produced by this invention were determined by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The article of the present invention is prepared by a process using accelerants whereby the process provides a commercially acceptable continuous CVD deposition of oxide films on moving glass, especially on a modern float-glass line, where the batch processes of the prior art are entirely inapplicable.

The effects of added water and added phosphites and borates on the refractive index and deposition rate of TEOS-based mixed oxide films are shown in the following Tables. These results are contrasted to those in Tables IV and V, which show the effect of the additives oxygen and a Lewis acid.

Table I shows the effect of added water. As the water concentration is increased, regardless of the tin/silicon ratio or the gas velocity, the deposition rate increases to commercially significant levels. These rate increases are also accompanied by increases in refractive index. In the tables here, the reported deposition rates are approximate with a range of about seven percent, unless the rate is followed by an expressed ± uncertainty.

TABLE I

Effect of Water Concentration on Mixed Oxide Refractive Index and Deposition Rate

MBTC mol%	TEOS mol%	Water mol%	R.I.	Dep. Rate Å/sec
665°C glass temperature, 160°C system temperature, 50 l/min gas flow.				
0.71	0.71	0.00	1.54	25
0.71	0.71	0.15	1.73	340
0.71	0.71	0.24	1.74	400
665°C glass temperature, 160°C system temperature, 12.5 l/min gas flow.				
1.05	0.59	0.00	1.74	290
1.05	0.59	0.60	1.78	330
1.05	0.59	1.10	1.80	480

While 160°C is preferred, the system temperature can be from about 125 to about 200°C.

Table II shows the effects of added TEP and of mixtures of TEP and lower-alkyl borate esters such as triethyl borate (TEB). The results show that TEP is very effective in accelerating the deposition rates of the mixed-oxide films to a high rate at specific and controlled refractive-index values. Additions of TEB at low levels to the TEP resulted in an additional small increase in rate. As used in this specification, the term "high rate," as applied to the film deposition described herein, is greater than about 350Å/sec, and preferably about 400Å/sec or higher. All the films produced under the conditions of Table II were clear.

TABLE II

Effect of MBTC/TEOS/TEP Concentrations on Deposition Rate

%TEOS	%MBTC	%TEP	%TEB	R.I.	Dep. Rate Å/sec
0.80	0.16	-	-	1.69±.02	38± 3
0.80	0.11	0.76	-	1.58±.01	542± 8
0.80	0.16	0.76	-	1.60±.01	416±22
0.78	1.56	0.75	-	1.67±.01	505± 4
0.78	1.84	0.75	-	1.69±.01	476±45
0.28	1.56	0.36	-	1.73±.01	231±46
0.27	1.56	0.62	-	1.71±.01	381±15
0.27	1.56	0.75	-	1.70±.01	482± 6
0.27	1.56	0.75	-	1.70±.01	482±16
0.27	1.56	0.74	0.18	1.70±.02	492±13
0.79	0.16	0.76	0.19	1.59±.01	473±56

The glass temperature was 665°C, its speed, 0.56 m/sec; system temperature 160°C, air. MBTC, TEOS, and TEP or the mixture of TEP and TEB were injected separately into the vaporizer section of the coater. Each data point was the average of three samples. The dew point was from -74 to -78°C.

Table III shows the effect of added oxygen. Increasing the oxygen concentration increases the deposition rate significantly, but not to the levels needed for commercial application.

TABLE III

Effect of Oxygen Concentration On Mixed Oxide Refractive Index and Deposition Rate

MBTC mol%	TEOS mol%	Oxygen vol% of air	R.I.	Dep. Rate Å/sec
0.71	0.71	20	1.54	25
0.71	0.71	50	1.63	50
0.71	0.71	75	1.65	160
0.71	0.71	100	1.66	240

665°C glass temperature, 160°C system temperature, 50 *l*/min gas flow.

Table IV shows the effect of added Lewis acid, which in this case is excess MBTC. As the concentration increases, the rate increases, although not to the levels needed for commercial application.

Table IV

Effect of MBTC Concentration on Mixed Oxide Refractive Index and Deposition Rate

MBTC mol%	TEOS mol%	R.I.	Dep. Rate Å/sec
0.48	0.47	1.78	160
0.48+0.23	0.48	1.78	200
0.48+0.47	0.47	1.85	300

665°C glass temperature, 160°C system temperature, 50 l/min gas flow.

The data in the tables show that effective CVD of mixed oxide films can be achieved at commercial rates by the present invention, with concomitant control of refractive index. The following examples illustrate preferred embodiments of this invention.

Example 1

A square plate of soda-lime silica glass, 9 centimeters (cm.) on a side, was heated on a hot block to 665°C. A gas mixture of about 0.16 mol% MBTC, 0.80 mol% TEOS, 0.75 mol% TEP, and the balance hot air at 160°C was directed over the glass at a rate of 12.5 liters per minute (l/min) for about 10 seconds. The center of the glass surface was uniformly coated with a film which had a pale green color in reflected light. Using the Prism Coupler technique, the refractive index was found to be 1.60 and the thickness was about 4260 Å, corresponding to a deposition rate of about 426 Å/sec. Similarly deposited films have been shown to be amorphous by XRD, and to be composed of oxides of tin, silicon and phosphorus by XPS.

Example 2

A gas mixture of about 1.84 mol% MBTC, 0.78 mol% TEOS, 0.75 mol% TEP, and the balance hot air was directed over a glass surface in the same manner as described in Example 1. The resulting film had a pale magenta color in reflected light. The refractive index was found to be 1.68,

and the thickness was about 4930 Å, corresponding to a deposition rate of about 493 Å/sec. Similarly deposited films have been shown to be amorphous by XRD, and to be composed of oxides of tin, silicon and phosphorus by XPS.

Example 3

A gas mixture of about 1.22 mol% MBTC, 0.58 mol% TEOS, 1.09 mol% H_2O and the balance hot air was directed over a glass surface as described in Example 1, but for eight seconds. The resulting film had a green color in reflected light. The refractive index was found to be 1.78, and the film thickness was about 4650 Å, which corresponds to a deposition rate of about 580 Å/sec. From XRD analysis, similarly deposited films have been found to consist of collapsed tetragonal unit cells of tin oxide, indicating some solid-solution formation with silicon dioxide. XPS analysis shows that the films comprise oxides of tin and silicon.

Example 4

Each of the films described in Examples 1 through 3 was successively deposited for one second in ascending-index order. The multi-layer film was then overcoated with about 3200 Å of fluorine-doped tin oxide. This film construction provided a transparent article with essentially no reflected color under conditions of daylight illumination.

Example 5

A 9-cm. square of soda-lime silica glass was heated on a hot block to 665°C. A gas mixture of about 1.04 mol% MBTC in air at 160°C, and a gas mixture of 1.04 mol% TEOS and 0.20 mol% TEP in air at 160°C were directed through two microprocessor-controlled globe valves over the glass at a total flow rate of 12.5 *l*/min for 30 sec. The globe valves were simultaneously opened and closed at a programmed rate such that the gas composition impinging on the glass sample was continuously changed from a mixture of high TEOS/TEP and low MBTC to a mixture of low TEOS/TEP and high MBTC. The center of the glass surface was uniformly coated with a film consisting of oxides of tin, silicon and phosphorus as determined by XPS analysis. As the film thickness increased, the amount of tin gradually

increased, while the amount of silicon and phosphorus decreased. The refractive index was calculated from these data, and from data derived from standard films, and found to lie between 1.52 and 1.87. This film construction provided an article with essentially no reflected color when overcoated with fluorine-doped tin oxide.

Example 6

A gas mixture of about 0.16 mol% MBTC, 0.80 mol% TEOS, and the balance hot air was directed over a glass surface as described in Example 1 for about 60 seconds. The resulting film had a magenta color in reflected light, and a refractive index of 1.69. The film thickness was about 2260 Å, corresponding to a deposition rate of about 38 Å/sec.

Example 7

A 0.5-*l* clear-glass beverage bottle was rotated and heated to about 600°C in an oven over a three-minute period. The heated bottle was transferred into a coating chamber, where it was contacted with a vapor mixture of 0.16 mol% MBTC, 0.80 mol% TEOS, 0.75 mol% TEP, and the balance hot air at about 170°C for 10 sec. The resulting film was magenta-blue in color, and was uniformly distributed on the sidewalls of the container from shoulder to base. The deposition rate was estimated to be about 200 Å/sec from the film color, compared to about 50 Å/sec for the bottle coated only with the vapor mixture of MBTC and TEOS.

From a review of the foregoing tables and examples, those skilled in the art will realize that TEB, TEP, and water serve as accelerants in the CVD of oxide films on glass, and that TEP and TEB are synergistic in accelerating the deposition rate of TEOS and MBTC. Accelerants useful in this invention are chosen from the group consisting of borate and phosphite esters, alkyltin halides, and water.

While the composition of the present invention is preferably applied continuously to a moving glass substrate by methods known to those skilled in the art, the composition of this invention also has utility in batch processes. In application under conditions of continuous deposition, the composition is preferably maintained at temperatures below about 200°C, and more

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preferably below about 175°C, and applied to the glass moving at about 15 meters per second to provide deposition at a rate of at least 350Å/sec., and preferably at a rate of at least 400Å/sec.

Modifications and improvements to the preferred forms of the invention disclosed and described herein may occur to those skilled in the art who come to understand the principles and precepts hereof. Accordingly, the scope of the patent to be issued hereon should not be limited solely to the embodiments of the invention set forth herein, but rather should be limited only by the advance by which the invention has promoted the art.

WHAT IS CLAIMED IS:

1. A gaseous composition at a temperature below about 200°C at atmospheric pressure, adapted to deposit at least a first layer of tin oxide and silicon oxide onto glass at a rate of deposition greater than about 350Å/sec. at a temperature below about 200°C, at atmospheric pressure, wherein the composition comprises a precursor of tin oxide, a precursor of silicon oxide, an accelerant selected from the group consisting of organic phosphites, organic borates and water, and mixtures thereof, and a source of oxygen.

2. The composition of claim 1 wherein the substrate is transparent flat glass at a temperature of from about 450 to about 650°C.

3. The composition of claim 1 producing a glass article having essentially no reflected color in daylight.

4. The composition of claim 1 wherein the glass substrate is moving and the deposition is continuous.

5. The composition of claim 1 at a temperature below about 175°C.

6. The composition of claim 1 wherein the accelerant is triethyl phosphite.

7. The composition of claim 1 wherein the precursor of the tin oxide is R_nSnX_{4-n}, where R is a straight, cyclic, or branched-chain alkyl, or alkenyl of from one to about six carbons; phenyl, substituted phenyl, or $R'CH_2CH_2$-, where R' is MeO_2C-, EtO_2C-, CH_3CO-, or HO_2C-; X is selected from the group consisting of halogen, acetate, perfluoroacetate, and their mixtures; and where n is 0, 1, or 2.

8. The composition of claim 1 wherein the precursor of the tin oxide is an alkyltin halide.

9. The composition of claim 1 wherein the precursor of the tin oxide is an alkyltin chloride.

10. The composition of claim 1 wherein the precursor of the tin oxide is chosen from the group consisting of monobutylytin trichloride, dibutylytin dichloride, tributylytin chloride, and tin tetrachloride.

11. The composition of claim 1 wherein the precursor of silicon oxide is $R_mO_nSi_p$, where *m* is from 3 to 8, *n* is from 1 to 4, *p* is from 1 to 4, and

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R is independently chosen from hydrogen and acyl, straight, cyclic, or branched-chain alkyl and substituted alkyl or alkenyl of from one to about six carbons, and phenyl or substituted phenyl.

12. The composition of claim 1 wherein the precursor of silicon oxide is selected from the group consisting of tetraethylorthosilicate, diacetoxydi-t-butoxysilane, ethyltriacetoxysilane, methyltriacetoxysilane, methyldiacetoxylsilane, tetramethyldisiloxane, tetramethylcyclotetrasiloxane, dipinacoloxysilane, 1,1-dimethylsila-2-oxacyclohexane, tetrakis (1-methoxy-2-propoxy) silane, and triethoxysilane.

13. The composition of claim 1 wherein the precursor of silicon oxide is tetraethylorthosilicate.

14. The composition of claim 1 wherein the accelerant comprises triethyl phosphite.

15. The composition of claim 1 wherein the accelerant comprises triethyl phosphite and triethyl borate.

16. The composition of claim 1 wherein the rate of deposition is greater than about 400Å/sec.

17. The composition of claim 1 wherein the first layer is amorphous.

18. The composition of claim 1 wherein the first layer comprises a plurality of layers, and at least a second layer is deposited on the first layer.

19. The composition of claim 18 wherein the second layer comprises a tin oxide.

20. The composition of claim 18 wherein the second layer comprises a mixture of tin oxide and a fluorine compound.

21. The composition of claim 18 wherein the first layer has a refractive index which changes continuously between the substrate and the second layer.

22. The composition of claim 18 wherein the second layer comprises a doped tin oxide.

23. The composition of claim 18 wherein the second layer is deposited from a precursor mixture comprising monobutyltin trichloride and a fluorine-containing material.

24. The composition of claim 18 wherein the first layer is deposited from a precursor mixture comprising monobutyltin trichloride and tetraethyl orthosilicate in the presence of triethyl phosphite.

25. A gaseous composition adapted to deposit at least a first layer of tin oxide and silicon oxide onto glass at a temperature below about 200°C, at atmospheric pressure, by the method of depositing at least one amorphous layer onto glass at a rate greater than about 400Å/sec., the layer having a controlled index of refraction, by applying to the glass a mixture of a tin oxide precursor, a silicon oxide precursor, and at least one accelerant chosen from the group consisting of boron and phosphorus esters and water.

26. The composition of claim 25 applied by continuous chemical-vapor deposition of a mixture of monobutyltin trichloride, tetraethylorthosilicate and an accelerant onto a moving glass sheet, wherein the glass is at a temperature of from about 450 to about 650°C.